Adsorptive separation of methylalumoxane by mesoporous molecular sieve MCM-41

Tsuneji Sano,* Keiko Doi, Hitoshi Hagimoto, Zhengbao Wang, Toshiya Uozumi and Kazuo Soga

School of Materials Science, Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-1292, Japan. E-mail: t-sano@jaist.ac.jp

Received (in Cambridge, UK) 4th January 1999, Accepted 17th March 1999

Separation of methylalumoxane (MAO) by adsorption on siliceous porous materials with different average pore diameters has been carried out; polymerization of ethylene was conducted with Cp_2ZrCl_2 using the separated MAO as cocatalyst, it was found that the MAO adsorbed on MCM-41 with average pore size of *ca*. 25 Å is very effective for ethylene polymerization.

Methylalumoxane (MAO) generated by controlled hydrolysis of trimethylaluminium (TMA) is known to be a changeable mixture of oligomers owing to the coexistence of TMA. Although several structures have been proposed for MAO such as rings, clathrates and linear or branched chains, the detailed structure of active MAO remains ambiguous because of the multiple equilibria being present in the solution.[1–3]

Recently, heterogenization of the alumoxane structure has been widely studied by using a variety of porous materials such as amorphous silica gel, zeolite or siliceous mesoporous materials MCM-41 as carriers.[4] However, no report concerning the adsorptive separation of MAO by such porous materials has been published. From such a viewpoint, we have attempted to separate MAO with the use of typical porous inorganic materials having different pore sizes and tested them towards ethylene polymerization. From those results, we propose here the potential use of mesoporous molecular sieve MCM-41 for the separation of active MAO.

MCM-41 has a regular array of uniform unidimensional pores where diameter can be controlled by altering the alkyl chain length of the surfactant.[5] Siliceous MCM-41(*n*) [*n*; chain length of 10, 16 and 22] were prepared from surfactants of decyltrimethylammonium bromide, hexadecyltrimethylammonium bromide and docosyltrimethylammonium chloride.[6,7] A silicalite of a MFI type was prepared under conventional hydrothermal synthesis conditions. Amorphous silica gels (average pore diameter : grade P6 = 137 Å, P10 = 293 Å) were donated by Fuji Silysia Co. To prevent the reaction between MAO and the surface hydroxy groups in the carriers, these materials were silylated by refluxing for 8 h with trimethylchlorosilane as a silylating agent. Characterization of these materials was conducted by X-ray diffraction (Rigaku RINT 2000), FTIR (JEOL JIR-7000) and nitrogen adsorption (Belsorp 28SA).

MAO was purified by drying the commercial MAO (from Tosoh Akuzo Co.) *in vacuo* in order to remove the free TMA. The amount of TMA left in the purified MAO was estimated to be *ca*. 8 wt% by ^1H NMR (Varian Gemini 300).[8] Separation of MAO from the silylated porous materials was conducted as follows : 0.7 g of each carrier was added to 10 mmol (based on Al) of MAO in toluene (10 ml) and the mixture was left to stand at room temperature for 5 h. The solid fraction was separated by filtration and washed 3 times with 20 ml toluene, followed by drying at room temperature under vacuum. The concentrations of Al in both solution and solid fractions were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP, Seiko SPS7700) after decomposition of MAO with nitric acid. The concentrations of Zr were also analyzed by ICP.

Polymerization of ethylene was conducted at 40 °C for 10 min with Cp_2ZrCl_2 using the separated MAO as cocatalyst. The Al/Zr ratio in the feed was kept constant. Measured amounts of toluene and the separated MAO were introduced into a 300 ml glass reactor equipped with a mechanical stirrer at room temperature. After the reactor was heated to the polymerization temperature (40 °C), the MAO solution was saturated with ethylene. A given amount of Cp_2ZrCl_2 was then injected to initiate the polymerization reaction. Ethylene was continuously fed to the reactor to keep the pressure constant during polymerization. The polymerization reaction was terminated by adding acidified methanol (5 wt% HCl). The precipitated polymers were washed with fresh methanol and dried under vacuum at 60 °C for 6 h. The number-average molecular weight ($\overline{M}_n$) and molar mass distribution (MMD; $\overline{M}_w/\overline{M}_n$) of the polymers were measured at 145 °C by gel permeation chromatography (GPC; Senshu Scientific SSC7100) using *o*-dichlorobenzene as the solvent. The GPC was calibrated using polystyrene standards and the method of universal calibration.

The synthesized MCM-41(*n*) (specific BET surface area *ca*. 1000 $m^2 g^{-1}$) and silicalite (382 $m^2 g^{-1}$) had well defined structures, as demonstrated by their X-ray diffraction patterns. The loss of the 3740 cm^{-1} peak assigned to the isolated OH groups was observed in the FTIR spectra of the silylated materials. Although a slight reduction in the specific BET surface area and the pore size calculated by the Dollimore–Heal (D–H) method was observed for silylated materials, no structural degradation occurred. The amount of MAO adsorbed in the carrier strongly depended upon its pore diameter. MCM-41(10), MCM-41(16) and MCM-41(22) showed higher adsorption ability, while MAO was scarcely adsorbed by silicalite probably due to an insufficient pore size. The pore volume of the MAO-containing MCM-41(16) (0.495 $cm^3 g^{-1}$) was reduced to *ca*. three fifths of its original value.

Fig. 1 shows the correlation between the pore size of porous materials and the activity of ethylene polymerization when MAO left in the liquid phase was used as cocatalyst. Activity is defined as the yield of polyethylene (PE) calculated from the

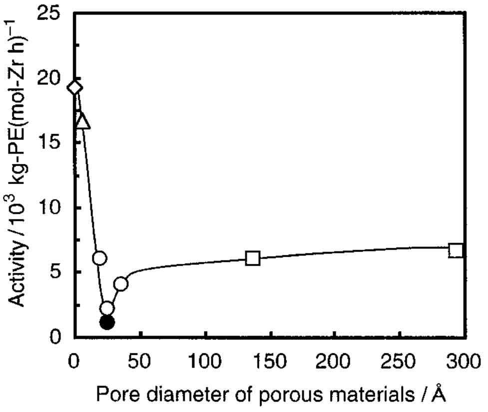

Fig. 1 Effect of pore diameter of porous materials on the initial activity of ethylene polymerization using the solution fraction. *Polymerization conditions*: T = 40 °C, Cp_2ZrCl_2 = 0.001 mmol, Al/Zr = 1000: (◇) ordinary MAO, (△) Silicalite, (○) MCM-41, (●) addition of TMA (1 mmol), (□) Silica gel.

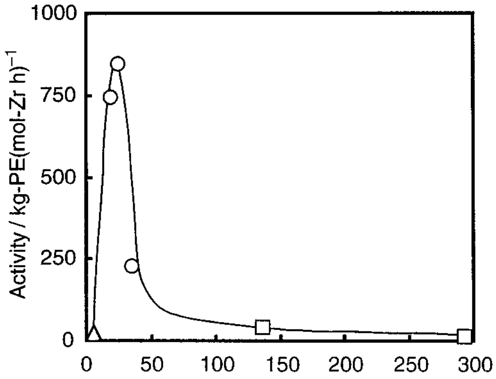

Fig. 2 Effect of pore diameter of porous materials on the initial activity of ethylene polymerization using the solid fraction. *Polymerization conditions*: T = 40 °C, Cp_2ZrCl_2 = 0.02 mmol, Al/Zr = 40: (△) Silicalite, (○) MCM-41, (□) Silica gel.

ethylene consumption at 10 min of the polymerization time. It was confirmed that the ethylene consumption measured by the flow meter agrees well with the polymer yield. The polymerization activity decreased drastically with increase in the pore diameter, and the minimum value was obtained at *ca.* 25 Å, suggesting that the MAO adsorbed on MCM-41 with an average pore size of *ca.* 25 Å is very effective for ethylene polymerization. Of course, we can not rule out a possibility that some factors other than the size of MAO affect the polymerization activity.

It is reported that some free TMA remains unremoved even when the MAO solution is dried under vacuum.[9,10] The residual TMA is considered to play an important role in the activation of metallocenes. Accordingly, it may be plausible to assume that such a marked decrease in the polymerization activity as observed in Fig. 1 is attributable to the reduction of free TMA. To clarify this point, ethylene polymerization was conducted by injecting additional TMA (1 mmol). The activity decreased slightly as shown in Fig. 1, indicating that the decrease in the activity is caused by some other factors.

Ethylene polymerization was then carried out using the solid fraction as cocatalyst. Prior to the polymerization, it was confirmed from the following experiments that the MAO once adsorbed in MCM-41(10), does not elute into the liquid phase during polymerization. The mixture of MAO-containing MCM-41(10) and Cp_2ZrCl_2 was brought into contact in toluene, and ethylene polymerization was conducted using the solution fraction as cocatalyst. However, only a trace amount of polymer was obtained. The degree of Al elution measured by elemental analysis of the solution fraction was *ca.* 1%. Fig. 2 shows the correlation between the pore size of porous materials and the polymerization activity, where the activity was evaluated on the basis of the amount of Cp_2ZrCl_2 occluded in the pores. The Al/Zr ratios in the solid were 70–90. In contrast to the results obtained by using the solution fraction (Fig. 1), the polymerization activity of the solid fraction was initially low and increased markedly, followed by a drastic decrease passing through a maximum value at *ca.* 25 Å. The result again supports the above assumption that the MAO adsorbed on MCM-41 with average pore size of *ca.* 25 Å is very effective for ethylene polymerization. Similar results have recently been reported by Van Looveren *et al.*[11] They studied the *in-situ* synthesis of MAO in the pores of MCM-41, and found that the $\{C_2H_4(1\text{-indenyl})_2\}Zr(CH_3)_2$ catalyst combined with the resulting MAO displays activity as high as the corresponding ordinary homogeneous catalyst system for ethylene–propylene co-oligomerization.

Table 1 Number-average molecular weight ($\overline{M}_n$) and molar mass distribution (MMD: $\overline{M}_w/\overline{M}_n$) of polyethylene obtained with various MAO materials.

Cocatalyst	Carrier	$10^{-3}\ \overline{M}_n$	$\overline{M}_w/\overline{M}_n$
MAO (solution fraction)	Silicalite	160	2.3
	MCM-41(10)	156	2.3
	MCM-41(16)	116	2.4
	MCM-41(22)	149	2.3
	Silica gel P6	178	2.1
	Silica gel P10	145	2.2
MAO (solid fraction)	MCM-41(10)	46	2.9
	MCM-41(16)	22	3.7
	MCM-41(22)	34	3.7
	Silica gel P6	7	6.6
Ordinary MAO		245	1.9

For reference, some analytical data of polyethylene obtained here are summarized in Table 1. The number-average molecular weights ($\overline{M}_n$) of polyethylene produced by the solution fraction are much higher as compared with those produced by the solid fraction. On the other hand, the molar mass distributions (MMD) of polyethylene produced by the solid fraction seem to be slightly broader. These results may suggest that the polymerization in MCM-41 is controlled by monomer (ethylene) diffusion through the pores which are sterically very crowded by MAO, Cp_2ZrCl_2 and produced polyethylene. A further study is now in progress to isolate the active MAO using the modified separation technology.

We thank Dr E. Kaji (Tosoh Akuzo Co.) for helpful discussions.

Notes and references

1 M. R. Mason, J. M. Smith, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 1993, **115**, 4971.

2 A. R. Barron, *Macromol. Symp.*, 1995, **97**, 15.

3 H. Shin, *Macromol. Symp.*, 1995, **97**, 27.

4 See for example; J. C. W. Chien and D. He, *J. Polym. Sci. Part A, Polym. Chem.*, 1991, **29**, 1603; K. Soga and M. Kaminaka, *Macromol. Chem. Rapid. Commun.*, 1992, **13**, 221; W. Kaminsky and F. Renner, *Macromol. Chem. Rapid. Commun.*, 1993, **14**, 239; F. Ciardelli, A. Altomare, G. Counti, G. Arribas, B. Mendez and A. Ismayel, *Macromol. Chem. Macromol. Symp.*, 1994, **80**, 29; T. Tudor and D. O'Hare, *Chem. Commun.*, 1997, 603.

5 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. MacCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10 834.

6 J. M. Kim. J. H. Kwak, S. Jun and R. Ryoo, *J. Phys. Chem.*, 1995, **99**, 16 742.

7 S. Namba, A. Mochizuki and M. Kito, *Stud. Surf. Sci. Catal.*, 1998, **117**, 257.

8 D. W. Imhoff, L. S. Simeral, S. A. Sangokoya and J. H. Peel, *Organometallics*, 1998, **17**, 1941.

9 W. Hagendorf, A. Harder and H. Sinn, *Macromol. Symp.*, 1995, **97**, 127.

10 I. Tritto, M. C. Sacchi and S. Li, *Macromol. Chem. Rapid. Commun.*, 1994, **15**, 217.

11 L. K. Van Looveren, D. F. Geysen, K. A. Vercruysse, B. H. Wouters, P. J. Grobet and P. A. Jacobs. *Angew. Chem., Int. Ed.*, 1998, **37**, 517.

Communication 9/00030E